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VACANCY RELAXATION IN CUBIC CRYSTALS

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Abstract—The configuration of the atoms surrounding a vacancy in four face-centered cubic and three body-centered cubic metals has been computed, using a pairwise, central-force model in which the energy of interaction between two atoms was taken to have the form of a Morse function. Only radial relaxations were considered. The first and second nearest-neighbor relaxations for the face-centered systems were found to be: Pb (1.42, -0.43), Ni (2.14, -0.39), Cu (2.24, -0.40) and Ca (2.73, -0.41, expressed in percentages of normal distances. For the body-centered systems the relaxations out to the fourth nearest neighbors to the vacancy were: Fe (6.07, -2.12, -0.25, —), Ba (7.85, -2.70, 0.70, -0.33) and Na (10.80, -3.14, 3.43, -0.20). The positive signs indicate relaxation toward the vacancy and the negative signs indicate relaxation away from the vacancy. The energies of relaxation (eV) are: Pb (0.162), Ni (0.626), Cu (0.560), Ca (0.400), Fe (1.410), Ba (0.950) and Na (0.172).

An estimate of the ease of motion of the atoms surrounding a vacancy in sodium was made, and it was concluded that NACHTRIEB's relaxation concept is probably valid in sodium.

1. INTRODUCTION

THEORETICAL studies of the geometrical configuration of the atoms surrounding vacancies in cubic crystals have recently been performed by several investigators. On the basis of a pairwise, central-force model for argon, KANZAKI⁽¹⁾ has computed the displacement of six sets of nearest neighbors from their normal lattice sites, using an inverse-power 6-10 potential for the interaction of two atoms. Detailed calculations for vacancy relaxation in a rare-gas-type crystal have also been performed by HALL⁽²⁾, using an inverse-power 6-12 potential. In an attempt to obtain results that could be applied to metals, GIRIFALCO and STREETMAN⁽³⁾ computed the lattice distortion around a vacancy in a body-centered crystal whose atoms interact according to an inverse-power 5-7 potential. The 5-7 potential energy function has been shown by FÜRTH to describe adequately the macroscopic properties of molybdenum, chromium and tungsten.⁽⁴⁾ HUNTINGTON and SEITZ⁽⁵⁾ and TEWORDT⁽⁶⁾ have used a non-pairwise approach in their calculations for copper.

The purpose of the present paper is to compute the configuration of the atoms around a vacancy in cubic metals in such a way as to retain the

simplicity of the pairwise interatomic potential approach, while minimizing the shortcomings encountered in the previous attempts. These shortcomings are that:

(1) The results of KANZAKI⁽¹⁾ and of HALL⁽²⁾ are applicable only to inert-gas crystals and should not be extrapolated to metals.

(2) The inverse-power 5-7 potential is inconsistent with the Born stability criteria for body-centered cubic crystals.⁽⁷⁾

Recently it has been shown that pairwise Morse potentials can be constructed that adequately reproduce the energy of cohesion, lattice parameter, compressibility and equation of state of metals.⁽⁸⁾ Furthermore, the Born stability criteria are satisfied for both face-centered and body-centered crystals whose atoms interact according to a Morse potential, and, although the pairwise calculations lead to the Cauchy relations which are not satisfied in metals, the magnitude of the agreement between the experimental and theoretical elastic constants is satisfactory. Thus, calculations based on Morse potentials should give results for metals that are more reliable than those previously obtained by using other types of pairwise force laws.

2. THE MORSE POTENTIAL FUNCTION

The interaction energy, ϕ_{ij} , of a pair of isolated particles i and j , interacting by means of a Morse potential, is:

$$\phi_{ij} = D[\exp\{-2\alpha(r_{ij}-r_0)\} - 2\exp\{-\alpha(r_{ij}-r_0)\}] \quad (1)$$

where D is the dissociation energy of the pair, r_0 is the equilibrium separation, r_{ij} is the actual separation and α is a constant.

The equation for the energy of interaction of one atom i with every other atom j in the crystal is:

$$\phi_i' = D[\sum_j \exp\{-2\alpha(r_j-r_0)\} - 2\sum_j \exp\{-\alpha(r_j-r_0)\}] \quad (2)$$

It is convenient at this point to define the following terms:

$$\beta = \exp(\alpha r_0)$$

$$r_j = (m_j^2 + n_j^2 + l_j^2)^{1/2}a$$

where l , m , n are position indices of the atoms in the crystal, and a is the half-cell lattice spacing.

$$\phi_i' = D\{\beta^2 \sum_j \exp(-2\alpha a[(m_j^2 + n_j^2 + l_j^2)]^{1/2}) - 2\beta \sum_j \exp(-\alpha a[(m_j^2 + n_j^2 + l_j^2)]^{1/2})\} \quad (3)$$

For the perfect crystal ϕ_i' is independent of i and is

$$\phi_i' = 2\Phi/N \quad (4)$$

where Φ/N is the energy of cohesion per atom.

Equation (3) holds for the case in which the origin of the coordinate system is a normal lattice site. To perform calculations about points other than normal lattice sites, it is necessary to translate the origin of the system. Thus, equations (1) and (3) are:

$$\begin{aligned} \phi_{ij} = D\{\beta^2 \exp(-2\alpha a[(m_j-\delta_1)^2 + (n_j-\delta_2)^2 + (l_j-\delta_3)^2]^{1/2}) - \\ 2\beta \exp(-\alpha a[(m_j-\delta_1)^2 + (n_j-\delta_2)^2 + (l_j-\delta_3)^2]^{1/2})\} \end{aligned} \quad (5)$$

$$\begin{aligned} \phi_i' = D\{\beta^2 \sum_j \exp(-2\alpha a[(m_j-\delta_1)^2 + (n_j-\delta_2)^2 + (l_j-\delta_3)^2]^{1/2}) - \\ 2\beta \sum_j \exp(-\alpha a[(m_j-\delta_1)^2 + (n_j-\delta_2)^2 + (l_j-\delta_3)^2]^{1/2})\} \end{aligned} \quad (6)$$

where δ_1 , δ_2 and δ_3 are the position indices of the translated origin.

3. METHOD OF CALCULATION

To obtain the equilibrium configuration of the atoms about a vacancy after relaxation, a process of successive approximations is employed in which it is assumed that the atomic relaxation is radial. In this process, the energy of the first nearest neighbors to the vacancy is found as a function of the radial displacement of the whole set toward or away from the vacant site. Meanwhile, the other sets of neighbors are held in their normal lattice sites. The point of minimum energy is assumed to be the equilibrium position of the first nearest neighbors to the first approximation. Next, while the first nearest neighbors are held in their relaxed positions, a point of minimum energy is found for the second nearest neighbors in a similar manner. This procedure is repeated for successive sets of nearest neighbors until a set of atoms is found which has an energy minimum a negligible distance from its normal position. This completes the first approximation.

Because of the motion of the second and successive sets of neighbors, the equilibrium position of the relaxed first set of neighbors has been disturbed. A second approximation to the position of the first nearest neighbors is found by repeating the calculation using the first approximation of the relaxed positions as the normal positions in the second approximation. This is repeated for all sets of neighbors until the relaxed positions of the atoms do not change appreciably upon further approximation. The relaxing atoms have now taken the positions of lowest energy, and it is assumed that this is the final configuration of atoms about a vacancy after relaxation.

The energy of relaxation is the energy change that takes place during relaxation, that is, the energy of the crystal before relaxation less the energy of the crystal after relaxation.

All calculations were performed over a cubic lattice having twenty atoms on a side. A crystal of this size acts as an infinite lattice for calculations done near the center of the lattice. A coordinate system is constructed with axes parallel to the cubic axes of the lattice and with the origin at the vacant site, which is located in the center of the lattice. Then, in order to perform summations about

any point in the system, the origin is translated to a point $\delta_1, \delta_2, \delta_3$.

The energy of an atom i in the lattice consists of the following terms:

(1) The energy of interaction of atom i with every other atom in the lattice which has not relaxed. This is found by means of equation (6), where l, m and n are limited to the position indices of every atom in the lattice that has not yet been relaxed, and δ_1, δ_2 and δ_3 are the position indices of atom i in the original coordinate system.

(2) The energy of interaction of atom i with all sets of relaxed neighbors other than the set to which the atom i belongs. Equation (6) is used here also, with the values of l, m and n limited to the position indices of the atoms concerned.

(3) One half of the energy of interaction of atom i with the other atoms in the same set of neighbors as the atom i . Equation (6) is again used here, with l, m and n limited to the position indices of the atoms concerned. The factor one-half must be included because the interactions between the atoms of the relaxing set are counted twice, and thus must be divided by two.

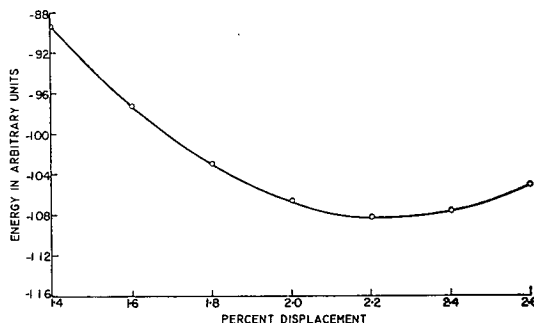


FIG. 1. A plot of energy against displacement for a first nearest-neighbor approximation in copper.

Since each of the atoms belonging to a certain set of neighbors has an equivalent environment, the energy of a set of neighbors may be found by calculating the energy of one atom in the set and multiplying it by the number of atoms in the set.

The equilibrium position and energy of an atom are found by plotting the energy of this atom against displacement as the atom is moved in increments radially toward or away from the vacancy, and selecting the displacement of minimum energy as

the equilibrium displacement. An example of such a plot is given in Fig. 1.

In this manner the equilibrium configuration and energy is found for each set of relaxing neighbors in turn. This process is repeated, as outlined previously, until a steady-state condition is reached.

4. ENERGY OF RELAXATION

The energy of relaxation is the energy of the crystal before relaxation less the energy of the crystal after relaxation. If E^U is the energy of interaction between the relaxing atoms in their normal lattice positions and the rest of the lattice, E^R is the energy of interaction between the relaxing atoms at their relaxed positions and the rest of the lattice and E^L is the energy of interaction among all the atoms in the crystal which do not change position during relaxation, then the energy of relaxation, E , is:

$$E = E^U + E^L - E^R - E^L = E^U - E^R$$

For face-centered cubic lattices:

$$E^U = 12\epsilon_1^U + 6\epsilon_2^U - \phi^U$$

$$E^R = 12\epsilon_1^R + 6\epsilon_2^R - \phi^R$$

For body-centered cubic lattices:

$$E^U = 8\epsilon_1^U + 6\epsilon_2^U + 12\epsilon_3^U + 24\epsilon_4^U - \phi^U$$

$$E^R = 8\epsilon_1^R + 6\epsilon_2^R + 12\epsilon_3^R + 24\epsilon_4^R - \phi^R$$

where

ϵ_n^U is the energy of an n th neighbor in its normal position,

ϵ_n^R is the energy of an n th neighbor in its relaxed position.

ϕ^U and ϕ^R are interaction energies between sets of neighbors in the unrelaxed and relaxed positions, respectively, which have been counted twice and, therefore, must be subtracted.

For face-centered lattices:

$$\phi^U = \phi(1,2)$$

$$\phi^R = \phi(1',2')$$

For body-centered lattices:

$$\begin{aligned} \phi^U = & \phi(1,2) + \phi(1,3) + \phi(1,4) + \phi(2,3) + \phi(2,4) + \\ & + \phi(3,4) \end{aligned}$$

$$\phi^R = \phi(1',2') + \phi(1',3') + \phi(1',4') + \phi(2',3') + \\ + \phi(2',4') + \phi(3',4')$$

The terms $\phi(m,n)$ and $\phi(m',n')$ are the sums of the interaction energies between all the atoms in neighbor set m and all the atoms in neighbor set n , all in their unrelaxed and relaxed positions, respectively.

5. RESULTS AND DISCUSSIONS

The results of the configuration calculations are given in Table 1 for both body-centered and face-centered metals. The summation in equation (6)

Table 1. Relaxed configuration of atoms about a vacancy in percent of normal distance from the vacancy. Negative values refer to motion away from the vacancy

	1st	2nd	3rd	4th
Pb	1.42	-0.43	—	—
Ni	2.14	-0.39	—	—
Cu	2.24	-0.40	—	—
Ca	2.73	-0.41	—	—
Fe	6.07	-2.12	-0.25	—
Ba	7.85	-2.70	0.70	-0.33
Na	10.80	-3.14	3.43	-0.20

F.c.c.

B.c.c.

and other numerical calculations were performed on a high-speed digital computer. A list of the constants used in the calculations is compiled in Table 2.

It will be noted that the magnitude of relaxation in the Morse crystal is not very large, the nearest-neighbor relaxation averaging about 2 per cent for the face-centered and about 8 per cent for the body-centered metals. Also, it was only necessary to calculate out to the second nearest neighbors in the face-centered case, though the fourth nearest neighbors had to be considered in the cases of body centered barium and sodium.

The highly relaxed configurations in the body-centered metals relative to the face-centered metals is a result of the combined effect of the open

Table 2. List of constants used in the Morse potential function
(See Ref. 8)

	β	$\alpha(\text{\AA}^{-1})$	$D(\text{eV})$	$r_0(\text{\AA})$
Pb	83.02	1.1836	0.2348	3.733
Ni	51.78	1.4199	0.4205	2.780
Cu	49.11	1.3588	0.3429	2.866
Ca	39.63	0.80535	0.1623	4.569
Fe	51.97	1.3885	0.4174	2.845
Ba	34.12	0.65698	0.1416	5.373
Na	23.28	0.58993	0.06334	5.336

body-centered structure and the long-range repulsions exhibited by the Morse function in body-centered crystals.

The energies of relaxation are tabulated in Table 3. These energies, being a fraction of an electron volt, are small compared to the energies of vaporization.

Table 3. The energy of relaxation, E , (eV)

	$E(\text{eV})$
Pb ..	0.162
Ni ..	0.626
Cu ..	0.560
Ca ..	0.400
Fe ..	0.410
Ba ..	0.950
Na ..	0.172

Another notable point is that the relaxation process in the Morse lattice is a complicated one, involving the inward (toward the vacancy) relaxation of some sets of neighbors and the outward relaxation of some other sets. This is in essential agreement with the results obtained from previous pairwise model calculations, but it is in disagreement with the work of TEWORDT in that his calculations show an inward motion of the second nearest neighbors in the case of copper. This discrepancy arises from the use of the pairwise Morse potential, in which the effects of the electron gas are neglected.

It should be noted that the Morse functions used in these calculations were derived from macroscopic data and reflect the electron distribution of

the perfect crystal. It is not known how the redistribution of the conduction electrons on forming a vacancy affects the constants in the Morse function.

The large relaxations in the case of sodium require comment. It has been suggested on the basis of diffusion experiments that the atoms surrounding vacancies in sodium are highly relaxed and have a density and energy content characteristic of the liquid phase.⁽⁹⁾ The atom movement within this relaxed structure, called a "relaxion", is assumed to be similar to that occurring in a liquid. The theoretical calculations show that the vacancy relaxation is most extensive in sodium. In order to decide whether or not the relaxion exists in sodium, some measure of the ease of motion of the atoms in the relaxed structure is needed. In the present investigation, the activation energy for the rotation of the cube formed by the eight nearest neighbors to the vacancy was taken to be a measure of the internal mobility of the atoms surrounding the vacancy. In calculating this activation energy, the saddle point configuration was assumed to be one in which the nearest-neighbor cube was rotated by 45° about a cubic axis. The volume of the cube was assumed to be the same in the saddle point and in the initial relaxed position. Using the Morse potential for sodium, the energy barrier for this model was found to be 0.70 eV. This number is certainly an overestimate, since further relaxation in the activated position was ignored. Furthermore, some other rotation model, such as rotation about a body diagonal, or rotation of a ring of four atoms might have a lower activation energy than 0.35 eV. It can be concluded, therefore, that the atoms around a vacancy in sodium have an

appreciable mobility and the present work supports NACHTRIEB's suggestion that a relaxion exists in this system. It seems unlikely, however, that the relaxion would exist in the face-centered metals or in those body-centered metals for which the nearest-neighbor relaxations are much less than that for sodium.

6. SUMMARY AND CONCLUSIONS

The configuration of atoms about a vacancy and the energy of relaxation for several body-centered and face-centered cubic metals were computed from Morse potentials and found to be in essential agreement with previous calculations. Although relaxation effects were found to be small, they were larger in the case of the body-centered metals than in the case of the face-centered metals.

Finally, an estimate was made of the ease of motion of the atoms surrounding a vacancy in sodium. The results show that NACHTRIEB's relaxion concept is probably valid in the case of sodium but not valid in those solids for which the relaxations are small.

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